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Abstract:

The present invention relates to a method for producing an aluminum nitride ceramic having a high thermal conductivity ratio. The method comprises the following steps: providing an aluminum nitride powder as a raw material; adding into the raw material an admixture of sintering aids selected from  $\text{Dy}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{B}_2\text{O}_3$ , and the like; blending the resulting mixture uniformly to form an AlN mixture; adding a binder, a dispersant, a plasticizer, and the like into the AlN mixture; making the AlN mixture into an AlN green body by means of dry-pressing or tape-casting techniques; after removing the binder from the green body, placing the green body into a graphite furnace into which a flowing nitrogen as a protection atmosphere is fed; sintering the green body at a temperature ranging from  $1550^\circ\text{C}$  to  $1800^\circ\text{C}$ ; and keeping the temperature for 2~6 hours to produce thereby a high-density AlN ceramic. The method of the present invention has the advantages of being a simple process, with the sintering step easily controlled and the resulting substrate being flat and smooth, etc.

## What claimed is:

1. A method for producing an aluminum nitride ceramic with high thermal conductivity comprising the following steps:

(1) Formulating an AlN mixture by:

a: employing AlN powders as a raw material, which has an average granule diameter of 0.2-3.0 $\mu$ m, oxygen content of 1.2 wt% or less, nitrogen content of 33.0 wt% or more, and carbon content of 0.06 wt% or less; and

b: adding an admixture of sintering aids into the AlN powders wherein the admixture is a combination of two or three of the following compounds: a rare earth metal oxide or fluoride, an alkali earth or alkali metal oxide, and an oxide of the III group elements, resulting in a formulation of:

the rare earth metal oxide or fluoride: 0~10.0 wt%

the alkali earth or alkali metal oxide: 0~6.0 wt%

the oxide of the III group elements: 0~6.0 wt%

the AlN powders: balance amount

wherein the rare earth metal oxide or fluoride is any one of  $Y_2O_3$ ,  $Dy_2O_3$ ,  $Sm_2O_3$ , and  $YF_3$ ; the alkali earth or alkali metal oxide is CaO or  $Li_2O$ , and the oxide of the III group elements is  $B_2O_3$  or  $Ga_2O_3$ ;

(2) Making an AlN body by:

a: fabricating an AlN green body by dry-pressing process which is accomplished by firstly adding a binder of polyvinyl alcohol (PVA) or polyvinyl butyral (PVB) into the AlN mixture obtained from the step (1) at a ratio of the mixture to the binder being 1:0.03~0.05; granulating the resulting mixture and then molding the granules into the AlN green body under a pressure of 90-100MPa;

b: fabricating an AlN tape body by a cast molding process which is accomplished by firstly adding a solvent, a dispersant, a plasticizer, and a binder into the AlN mixture obtained from the step (1) to form a cast slurry having a composition of:

the solvent: 32~45 wt%

the dispersant: 1~3 wt%

the plasticizer: 0.5~2wt%

the binder: 5~7 wt%

the AlN mixture: balance amount

wherein the solvent is any one of ethanol, ethyl butyl ketone and cyclohexanone;

the dispersant is glycerin trioleate or fish oil; the plasticizer is dibutyl phthalate; and the binder is polyvinyl butyral (PVB);

(3) Burning off the binder from the resulting AlN body by:

(a): burning off the binder from the AlN green body within an atmosphere furnace at a temperature from room temperature to 600°C with air being the atmosphere wherein the temperature increases at a rate of 0.4~0.6°C per minute, and then at a temperature from 600°C to 1150°C with a flowing nitrogen gas being the protecting atmosphere wherein the temperature increases at a rate of 2~3°C per minute;

(b): burning off the binder from the AlN tape body within an atmosphere furnace at a temperature from room temperature to 600°C with air being the atmosphere wherein the temperature increases at a rate of 0.2~0.3°C per minute, and then at a temperature from 600°C to 1150°C with a flowing nitrogen gas being the protecting atmosphere wherein the temperature increases at a rate of 2~3°C per minute;

(4) Putting the AlN body resulted from the binder-bruning off step into a graphite furnace feeding with a flowing nitrogen gas, then sintering the body at a temperature of 1550°C~1800°C for 2~6 hours, and obtaining a high-density AlN ceramic thereby.

## **A Method for Producing an Aluminum Nitride Ceramic with High Thermal Conductivity Ratio**

The present invention belongs to a field of material technology, and specifically relates to a method for producing an aluminum nitride ceramic with high thermal conductivity ratio.

With rapid development of the micro-electronics technology, the substrate plate used as an electric-insulating material is required to possess higher thermal conductivity ratio and a distinguished dielectric performance. AlN has become a new generation of the high-density packaging material due to its high thermal conductivity capability, the adaptation of its thermal expansion coefficient to that of Si and GaAs, and its excellent mechanical and electronic performances. However, AlN is difficult to be sintered because it is a covalent complex bonded by a covalent linkage; furthermore, owing to the strong affinity between AlN and  $\text{Al}_2\text{O}_3$ , an AlN powder usually contains  $\text{Al}_2\text{O}_3$ , and consequently, the oxygen in the AlN powder will greatly reduce the intrinsic thermal conductivity of AlN and thereby will cause a defect with respect to lattice of the complex. Therefore, in the prior manufacturing processes, a certain amount of an alkali earth metal oxide or a rare earth metal oxide such as CaO,  $\text{Y}_2\text{O}_3$ , or the like is used as a sintering aid and added into an AlN mixture. For either of the substrate plate made by dry-press molding process and the substrate made by cast molding process, the AlN mixture is sintered at a high temperature ranging from  $1850^\circ\text{C}$  to  $1900^\circ\text{C}$  for 2~6 hours in a furnace feeding with a flowing  $\text{N}_2$  gas or the like as a protecting atmosphere. The disadvantages of this prior process include that it is difficult to be applied to a metallized co-sintering process because of the high temperature adopted in the sintering step and that the smoothness and roughness of the substrate is not easy to control.

The object of the present invention is to provide a new method for producing an aluminum nitride ceramic with high thermal conductivity ratio, comprising the step of adding a sintering aid in the sintering process to reduce the sintering temperature and to render the sintering process easily controlled. In particular, by the method of the present invention, the densification could be also achieved at a lower sintering temperature even if an AlN powder having a bigger average particle diameter is employed as a raw material.

The method of the present invention for producing an aluminum nitride ceramic

with high thermal conductivity comprises of the following steps:

(1) Formulating an AlN mixture by:

a: employing AlN powders as a raw material, which has an average granule diameter of 0.2-3.0 $\mu$ m, oxygen content of 1.2 wt% or less, nitrogen content of 33.0 wt% or more, and carbon content of 0.06 wt% or less; and

b: adding an admixture of sintering aids into the AlN powders wherein the admixture is a combination of two or three of the following compounds: a rare earth metal oxide or fluoride, an alkali earth or alkali metal oxide, and an oxide of the III group elements, resulting in a formulation of:

the rare earth metal oxide or fluoride: 0~10.0 wt%

the alkali earth or alkali metal oxide: 0~6.0 wt%

the oxide of the III group elements: 0~6.0 wt%

the AlN powders: balance amount

wherein the rare earth metal oxide or fluoride is any one of  $Y_2O_3$ ,  $Dy_2O_3$ ,  $Sm_2O_3$ , and  $YF_3$ ; the alkali earth or alkali metal oxide is CaO or  $Li_2O$ , and the oxide of the III group elements is  $B_2O_3$  or  $Ga_2O_3$ ;

(2) Making an AlN body by:

a: fabricating an AlN green body by dry-pressing process which is accomplished by firstly adding a binder of polyvinyl alcohol (PVA) or polyvinyl butyral (PVB) into the AlN mixture obtained from the step (1) at a ratio of the mixture to the binder being 1:0.03~0.05; granulating the resulting mixture and then molding the granules into the AlN green body under a pressure of 90-100MPa;

b: fabricating an AlN tape body by a cast molding process which is accomplished by firstly adding a solvent, a dispersant, a plasticizer, and a binder into the AlN mixture obtained from the step (1) to form a cast slurry having a composition of:

the solvent: 32~45 wt%

the dispersant: 1~3 wt%

the plasticizer: 0.5~2wt%

the binder: 5~7 wt%

the AlN mixture: balance amount

wherein the solvent is any one of ethanol, ethyl butyl ketone and cyclohexanone; the dispersant is glycerin trioleate or fish oil; the plasticizer is dibutyl phthalate or dibutyl titanate; and the binder is polyvinyl butyral (PVB);

(3) Burning off the binder from the resulting AlN body by:

(a): burning off the binder from the AlN green body within an atmosphere furnace at a temperature from room temperature to 600°C with air being the atmosphere wherein the temperature increases at a rate of 0.4~0.6°C per minute, and then at a temperature from 600°C to 1150°C with a flowing nitrogen gas being the protecting atmosphere wherein the temperature increases at a rate of 2~3°C per minute;

(b): burning off the binder from the AlN tape body within an atmosphere furnace at a temperature from room temperature to 600°C with air being the atmosphere wherein the temperature increases at a rate of 0.2~0.3°C per minute, and then at a temperature from 600°C to 1150°C with a flowing nitrogen gas being the protecting atmosphere wherein the temperature increases at a rate of 2~3°C per minute;

(4) Putting the AlN body resulted from the binder-burning off step into a graphite furnace feeding with a flowing nitrogen gas, then sintering the body at a temperature of 1550°C~1800°C for 2~6 hours, and thereby obtaining a high-density AlN ceramic.

Due to the following properties and characteristics, the admixture of sintering aids employed in the present invention brings advantages, including, that the sintering temperature can be chosen within a wide range, especially that the densification sintering can be accomplished at a lower temperature, to obtain an AlN ceramic having high and excellent performances which is more applicable in high-density packaging technology.

1. The admixture of sintering aids employed in the present invention has a low eutectic liquid phase point that may be controlled within a temperature range of 1350~1500°C. Therefore, in the method of the present invention, the sintering densification and the growth of crystal grains of the AlN ceramic are mainly controlled by the liquid phase and thus, the sintering is easier to be controlled. This principle is different from the one of the conventional methods where the sintering is proceeded at a high temperature. In the conventional methods, the sintering densification and the growth of crystal grains of the AlN ceramic are mainly controlled by diffusion. In particular, by the method of the present invention, the densification could be also achieved at a lower sintering temperature even if an AlN powder having a bigger average particle diameter is employed as a raw material.

2. The admixture of sintering aids employed in the present invention does not have chemical activities causing the admixture to react with the AlN. So, the crystal morphology of the AlN appears to be a polyhedral, the growth of crystal grains is

perfect, and the crystal grains contact with each other by surface to surface. As a result, the cross section for thermal conducting is large, which is favor of improving the thermal conductivity of the AlN ceramic.

3. The eutectic liquid phase, formed by the admixture of sintering aids employed in the present invention, has a lower liquid phase point, resulting in a better flowability of the liquid phase. So, being promoted by the impetus produced during the grain growth, the crystal grains will retract to form triangle grain boundaries, and the occurrence of the second phase between the crystal grains will be reduced, which is favor of improving the thermal conductivity of the AlN ceramic.

4. Some compositions of the admixture of sintering aids employed in the present invention have a much lower free energy ( $\Delta G^\circ$ ) for generating aluminates, consequently they could react with  $\text{Al}_2\text{O}_3$  to form aluminates at a lower sintering temperature. The crystal structures of the aluminates are mainly garnet crystals of cubic crystal system with excellent crystallizing capabilities. Therefore, the lattice oxygen can be easily and potently removed from the AlN crystal at a lower temperature, which is also favor of improving the thermal conductivity of the AlN crystal grains.

5. During the step of sintering, some components of the admixture of sintering aids employed in the present invention may be volatilized as they are, or may be volatilized as a nitride, or be transformed into a solid solution of an aluminate, depending on the variety of the formulation of the admixture. All these play a role in refining grain boundaries and thereby improving the thermal conductivity of the AlN ceramic.

Due to the above-mentioned characteristics of admixture of sintering aids employed in the present invention, the sintering temperature could be within a range of  $1550^\circ\text{C}\sim 1800^\circ\text{C}$ , i.e. decreasing by  $200\sim 350^\circ\text{C}$  as compared with the temperature at which an AlN ceramic is sintered in a prior process. As a result, the method of the present invention has the advantages of being a simple process, with the sintering step easily controlled and the resulting substrate being flat and smooth, etc. Moreover, owing to this lower sintering temperature, the method of the present invention can guarantee the properties of a substrate plate (or substrate sheet) with respect to smoothness and roughness. On the other hand, it is easily to be co-sintered with a metal. These characteristics of the thus obtained substrate are substantially similar to those of  $\text{Al}_2\text{O}_3$  substrate that is currently widely employed in micro-electronics

packaging technology. However, the AlN ceramic obtained by the method of the present invention possesses the following properties: a thermal conductivity of 80~200W/m.k, a tearing resistance of 300MPa or more, a dielectric constant of 8.5~9.5, a dielectric loss of  $30.0\sim4.0\times10^{-4}$ , and a thermal expansion coefficient of  $4.3\sim4.6\times10^{-6}/^{\circ}\text{C}$ , which are much more superior than the properties of  $\text{Al}_2\text{O}_3$  substrate. Therefore, the present invention will facilitate the application of an AlN ceramic in the high-density packaging technology.

The present invention is described in a way of specific examples hereinafter:

(One) Preparation of AlN Ceramic Substrate Plate by Dry-press process

An AlN mixture, having a average granule diameter of  $2.5\mu\text{m}$ , oxygen content  $\leq 1.1\text{ wt\%}$ , nitrogen content  $\geq 33.3\text{ wt\%}$ , carbon content  $\leq 0.03\text{ wt\%}$ , is used as a raw material. A certain amount of an admixture of sintering aids such as  $\text{Y}_2\text{O}_3\text{-B}_2\text{O}_3$  or  $\text{Dy}_2\text{O}_3\text{-CaO}$ , or the like is added into the raw material. The formulation is given in following Table 1.

**Table 1. Formulation of the AlN ceramic , Sintering Parameters, and Thermal Conductivity of the AlN Ceramic**

Sample No.	Composition						Binder		Sintering Parameters		Thermal Conductivity
	AlN	$\text{Y}_2\text{O}_3$	$\text{Dy}_2\text{O}_3$	CaO	$\text{Ga}_2\text{O}_3$	$\text{B}_2\text{O}_3$	PVA	PVB	T( $^{\circ}\text{C}$ )	Time (h)	(w/mk)
1	96	1.6	/	/	/	2.4	0.04	/	1800	4	189
2	96	2.0	/	/	2.0	/	/	0.035	1750	4	137
3	94	1.0	2.5	/	/	2.5	/	0.05	1650	4	146
4	94	/	3.2	1.0	1.8	/	/	0.04	1650	4	156

An absolute ethanol is added into the formulated mixture and the resulting mixture is blended in a ball-mill for 48 hours. The mixture is dried and sieved in the same way as the conventional method for producing a ceramic. Then, a small amount of polyvinyl alcohol (PVA) or polyvinyl butyral (PVB) as a binder is added into the sieved material, and mixed uniformly. After being granulated, the mixture was formed into a green body with a desired shape and dimensions by dry-pressing process. The green body shall be subjected to a step of burning off the binder, which is accomplished in an atmosphere furnace at a temperature from room temperature to  $600^{\circ}\text{C}$  with air being the atmosphere wherein the temperature is controlled to increase



at a rate of  $0.4\sim 0.6^{\circ}\text{C}$  per minute depending on the thickness of the green body, and then at a temperature from  $600^{\circ}\text{C}$  to  $1150^{\circ}\text{C}$  with a flowing nitrogen gas being the protecting atmosphere wherein the temperature is controlled to increase at a rate of  $2\sim 3^{\circ}\text{C}$  per minute.

After the step of burning off the binder, the AlN green body is put into a graphite furnace and sintered therein while a flowing nitrogen gas is employed as a protecting atmosphere. As to the temperature and time for sintering, as well as the thermal conductivity of the sintered product, please refer to the above Table 1.

#### (Two) Preparation of AlN Ceramic Substrate by Cast Molding Process

An AlN mixture, having a average granule diameter of  $2.5\mu\text{m}$ , oxygen content  $\leq 1.1\text{ wt\%}$ , nitrogen content  $\geq 33.3\text{ wt\%}$ , carbon content  $\leq 0.03\text{ wt\%}$ , is used as a raw material. A certain amount of an admixture of sintering aids such as  $\text{Y}_2\text{O}_3\text{-B}_2\text{O}_3$  or  $\text{Dy}_2\text{O}_3\text{-CaO}$ , or the like is added into the raw material. The formulation is given in the above Table 1. According to the steps of a conventional method, a solvent, a dispersant, a binder and a plasticizer are added into the formulated mixture to form a casting slurry, and the slurry is blended for 24~48 hours. The composition of the slurry is given in the following Table 2.

The slurry is cast into a tape body having a desired thickness and dimension by using tape-casting molding machine, and the tape body is cut into a green body in a shape of sheet with certain dimensions. Then, the binder is burned off from the green body in an atmosphere furnace in accordance with a conventional method, wherein the binder is burned off in air at a temperature from room temperature to  $600^{\circ}\text{C}$  with the temperature increasing at a rate of  $0.4\sim 0.6^{\circ}\text{C}$  per minute, and then the body is biscuit-fired at a temperature from  $600^{\circ}\text{C}$  to  $1150^{\circ}\text{C}$  with a flowing nitrogen gas being the protecting atmosphere and with the temperature increasing at a rate of  $2\sim 3^{\circ}\text{C}$  per minute.

Following up the step of burning off the binder, the cast-molded AlN green body is put into a graphite furnace, and sintered therein at a temperature of  $1650^{\circ}\text{C}$  for a period of 4 hours while a flowing nitrogen gas is employed as a protecting atmosphere. The thermal conductivity of the resulted products is given in Table 2.

Table 2. Formulation and Thermal Conductivity of the Cast-molded AlN Ceramic

Sample No.	Composition of the AlN mixture (wt%)						Formulation of the slurry for cast molding (wt%)								Thermal Conductivity
	AlN	Dy <sub>2</sub> O <sub>3</sub>	CaO	Ga <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	the AlN Mixture	Solvent			Dispersant		Plasticizer		Binder	
							Ethanol	Cyclohexanone	Ethyl butyl ketone	Glycerin trioleate	Fish Oil	1*	2*		
1	94	3.5	1.5	2.0	/	59.6	/	33	/	1.2	/	/	0.8	5.4	135
2	94.5	4.0	1.0	0.5	/	50.3	/	/	40.5	/	2.3	/	1.1	5.8	125
3	94	3.6	0.5	/	1.4	58.5	/	34	/	1.2	/	0.7	/	5.6	130
4	94	4.0	1.0	/	1.0	57.3	18	/	17	/	1.25	1.2	/	5.25	140
5	95	3.0	2.0	/	/	55.8	16.8	18.2	/	/	1.4	/	1.2	6.6	123

1\* dibutyl titanate

2\* dibutyl phthalate



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[54]发明名称 高热导率氮化铝陶瓷的制造方法

[57]摘要

本发明涉及一种高热导率氮化铝陶瓷的制造方法。该方法以氮化铝粉体为原料，加入混合助烧结剂  $\text{Li}_2\text{O}_3$ 、 $\text{CaO}$ 、 $\text{B}_2\text{O}_3$  等，混均成为  $\text{AlN}$  混合料，然后在混合料中加入粘结剂、分散剂、增塑剂等以后，用干压法或流延法将混合料制成  $\text{AlN}$  坯体，最后将排胶后的  $\text{AlN}$  素坯置于石墨加热炉中，通以流动  $\text{N}_2$  气保护，在  $1550^\circ\text{C} \sim 1800^\circ\text{C}$  下烧结，保温 2~6 小时，即可获得高致密度  $\text{AlN}$  陶瓷。本发明具有工艺简单、烧结易于控制、基片平整光滑等优点。

# 权 利 要 求 书

1、一种高热导氮化铝陶瓷的制备方法,其特征在于该方法包括下列各步骤:

(1) 配制AlN混合料:

a. 采用平均粒径为 $0.2\sim 3.0\mu\text{m}$ 、氧含量 $\leq 1.2\text{wt}\%$ 、氮含量 $\geq 33.0\text{wt}\%$ 、碳含量 $\leq 0.06\text{wt}\%$ 的AlN粉体为原料;

b. 在上述AlN粉体中加入混合助烧结剂,混合助烧结剂为稀土金属氧化物或氟化物、碱土或碱金属氧化物以及Ⅲ族氧化物这三类化合物中的二种或三种的组合,其配比为:

稀土金属氧化物或氟化物:  $0\sim 10.0\text{wt}\%$ ,

碱土或碱金属氧化物:  $0\sim 6.0\text{wt}\%$ ,

Ⅲ族氧化物:  $0\sim 6.0\text{wt}\%$ ,

余为AlN粉体原料,

上述的稀土金属氧化物或氟化物为 $\text{Y}_2\text{O}_3$ 、 $\text{D}_{y2}\text{O}_3$ 、 $\text{Sm}_2\text{O}_3$ 、 $\text{YF}_3$ 中的任何一种,碱土或碱金属氧化物为 $\text{CaO}$ 或 $\text{Li}_2\text{O}$ ,Ⅲ族氧化物为 $\text{B}_2\text{O}_3$ 或 $\text{Ga}_2\text{O}_3$ ;

(2) 制备AlN坯体:

a. 用干压法制备AlN素坯:在上述第一步制成的AlN混合料中,加入粘结剂聚乙烯醇(PVA)或聚乙烯缩丁醛(PVB),混合料与粘结剂的比例为 $1:0.03\sim 0.05$ ,造粒后在 $90\sim 100\text{MPa}$ 压力下成型,即为AlN素坯;

(b) 用流延成型法制备AlN带坯:在上述第一步制成的AlN混合料中,加入溶剂、分散剂、增塑剂和粘结剂,制成流延浆料其配比为:

溶 剂:  $32\sim 45\text{wt}\%$

分散剂:  $1\sim 3\text{wt}\%$

增塑剂:  $0.5\sim 2\text{wt}\%$

粘结剂:  $5\sim 7\text{wt}\%$

全为AlN混合料;

上述的溶剂为乙醇、乙-丁酮或环己酮中的任何一种，上述的分散剂为三油酸甘油酯或鱼油，增塑剂为邻苯二甲酸二丁酯，粘结剂为聚乙烯缩丁醛 (PVB)；

(3) 对制备的AlN坯体进行排胶处理:

(a) 对AlN素坯排胶: 在气氛炉中排胶, 从室温至600℃在空气下进行, 升温速度为0.4~0.6℃/分, 600℃~1150℃在流动氮气保护气氛中进行, 升温速度控制在2~3℃/分;

(b) 对AlN带坯排胶: 在气氛炉中排胶, 从室温至600℃在空气中排胶, 升温速度控制在0.2~0.3℃/分, 600℃~1150℃在流动氮气保护气氛中进行, 升温速度为2~3℃/分;

(4) 将上述排胶后的AlN坯体置于石墨加热炉中, 通以流动氮气, 在1550℃~1800℃温度内进行烧结, 保温2—6小时, 即可获得高致密度AlN陶瓷。

## 高热导率氮化铝陶瓷的制造方法

本发明涉及一种高热导率氮化铝陶瓷的制造方法, 属材料技术领域。

随着微电子技术的迅速发展, 要求作为电绝缘材料的基板具有更高的热导率和优良的介电性能。由于AlN具有高的热传导性、与Si和GaAs相匹配的热膨胀系数和优良的机、电性能, 因而成为新一代的高密度封装材料。但是, AlN属共价键晶体, 难于烧结; 另一方面, 由于AlN与 $Al_2O_3$ 具有很强的亲合力, AlN粉体中往往含有 $Al_2O_3$ , 固溶在AlN中的氧导致晶格缺陷等而大大降低AlN的本征热导率。所以, 以往的制造工艺大多采用在AlN混合料中添加一定量的CaO或 $Y_2O_3$ 等碱土金属或稀土金属氧化物作为助烧结剂, 无论是干压成型的基板或流延成型的基片, 都采用在 $1850^{\circ}C \sim 1900^{\circ}C$ 的高温烧结工艺, 通以 $N_2$ 等保护气, 保温2—6小时。该工艺的缺点是烧结温度高, 给金属化共烧带来困难, 而且基片的平整度和粗糙度难于控制。

本发明的目的是设计一种新的高热导率氮化铝陶瓷的制造方法, 在烧结工艺中加入助烧结剂, 以降低烧结温度, 使烧结过程易于控制。尤其是当采用较大平均颗粒尺寸的AlN粉体原料时, 也能在较低的烧结温度下达到致密化烧结。

本发明的高热导氮化铝陶瓷的制备方法, 包括下列各步骤:

(1) 配制AlN混合料:

a. 采用平均料径为 $0.2 \sim 3.0 \mu m$ 、氧含量 $\leq 1.2 wt\%$ 、氮含量 $\geq 33.0 wt\%$ 、碳含量 $\leq 0.06 wt\%$ 的AlN粉体为原料;

b. 在上述AlN粉体中加入混合助烧结剂, 混合助烧结剂为稀土金属氧化物或氟化物、碱土或碱金属氧化物以及Ⅲ族氧化物这三类化合物中的二种或三种的组合, 其配比为:

稀土金属氧化物或氟化物:  $0 \sim 10.0 wt\%$ ,

碱土或碱金属氧化物: 0~6.0wt%,

Ⅲ族氧化物: 0~6.0wt%,

余为AlN粉体原料,

上述的稀土金属氧化物或氟化物为 $Y_2O_3$ 、 $Dy_2O_3$ 、 $Sm_2O_3$ 、 $YF_3$ 中的任何一种, 碱土或碱金属氧化物为CaO或 $Li_2O$ , Ⅲ族氧化物为 $B_2O_3$ 或 $Ga_2O_3$ ;

## (2) 制备AlN坯体:

a. 用干压法制备AlN素坯: 在上述第一步制成的AlN混合料中, 加入粘结剂聚乙烯醇(PVA)或聚乙烯缩丁醛(PVB), 混合料与粘结剂的比例为1:0.03~0.06, 造粒后在90—100MPa压力下成型, 即为AlN素坯;

(b) 用流延成型法制备AlN带坯: 在上述第一步制成的AlN混合料中, 加入溶剂、分散剂、增塑剂和粘结剂, 制成流延浆料, 其配比为:

溶 剂: 32~45wt%

分散剂: 1~3wt%

增塑剂: 0.5~2wt%

粘结剂: 5~7wt%

余为AlN混合料;

上述的溶剂为乙醇、乙-丁酮或环己酮中的任何一种, 上述的分散剂为三油酸甘油酯或鱼油, 增塑剂为邻苯二甲酸二丁酯或二丁基钛酸盐, 粘结剂为聚乙烯缩丁醛(PVB);

## (3) 对制备的AlN坯体进行排胶处理:

(a) 对AlN素坯排胶: 在气氛炉中排胶, 从室温至600℃在空气下进行, 升温速度为0.4~0.6℃/分, 600℃~1150℃在流动氮气保护气氛中进行, 升温速度控制在2~3℃/分;

(b) 对AlN带坯排胶: 在气氛炉中排胶, 从室温至600℃在空气中排胶, 升温速度控制在0.2~0.3℃/分, 600℃~1150℃在流动氮气保护气氛中进行, 升温速度为2~3℃/分;

(4) 将上述排胶后的AlN坯体置于石墨加热炉中, 通以流动氮气, 在 $1550^{\circ}\text{C} \sim 1800^{\circ}\text{C}$ 温度内进行烧结, 保温2—6小时, 即可获得高致密度AlN陶瓷。

本发明所采用的混合助烧结剂具有下述优点, 可在很宽的温度范围内选择某一烧结温度, 尤其是在较低的烧结温度下进行致密化烧结, 获得性能优良的AlN陶瓷, 更有利于在高密度封装技术中的应用。

1、本发明所采用的混合助烧结剂具有低的共溶液相点, 液相点可控制在 $1350 \sim 1500^{\circ}\text{C}$ , 因此AlN陶瓷的烧结致密化及晶粒长大过程主要受液相控制, 与以往的高温AlN陶瓷烧结机理主要受扩散控制有所不同, 烧结更易于控制。尤其当采用较大平均颗粒尺寸的AlN粉体原料时, 也能在较低的烧结温度下达到致密化烧结。

2、本发明所采用的混合助烧结剂不具有与AlN产生反应的化学活性, AlN的结晶形态表现为多面体形, 晶粒生长完善, 晶粒之间呈面接触, 热传导截面大, 有利于提高AlN陶瓷的热导率。

3、本发明所采用的混合助烧结剂所形成的低共熔液相具有较好的流动特性, 受AlN晶粒长大的推动力的作用可回缩到三角晶界, 从而减少晶间第二相, 有利于提高AlN陶瓷的热导率。

4、本发明所采用的混合助烧结剂中的某些组成, 具有更低的铝酸盐生成自由能 $\Delta G^{\circ}$ , 因此能在较低的烧结温度下与 $\text{Al}_2\text{O}_3$ 反应生成铝酸盐, 而且主要是具有立方晶系结构的石榴子石型结晶, 结晶能力强。因此在较低温度下具有较强的排除AlN中的晶格氧的能力, 有利于提高AlN晶粒的热导率。

5、本发明所采用的混合助烧结剂中的某些组成, 依据配方的不同, 在烧结过程中, 或本身可以挥发, 或形成氮化物挥发, 或固溶在铝酸盐中, 这些都起着净化晶界的作用, 可提高AlN陶瓷的热导率。

由于本发明采用了具有以上特点的混合助烧结剂, 与以往的AlN陶



瓷的制备工艺相比, 烧结温度可降低 $200\sim 350^{\circ}\text{C}$ 在 $1550^{\circ}\text{C}\sim 1800^{\circ}\text{C}$ , 达到致密烧结, 工艺简单, 烧结易于控制。同时, 由于烧结温度较低可以保证基板(基片)的平整度和粗糙度; 另一方面易于实现与金属共烧。这些工艺特点与目前在微电子封装技术中得到广泛应用的 $\text{Al}_2\text{O}_3$ 基片基本相似, 然而本发明所获得的 $\text{AlN}$ 陶瓷热导率可达 $80\sim 200\text{W/m}\cdot\text{k}$ , 抗拆强度 $> 300\text{MPa}$ , 介电常数 $8.5\sim 9.5$ , 介质损耗 $30.0\sim 4.0\times 10^{-4}$ , 热膨胀系数 $4.3\sim 4.6\times 10^{-6}/^{\circ}\text{C}$ , 这些性能均比 $\text{Al}_2\text{O}_3$ 陶瓷基片优异得多, 因此本发明更有利于 $\text{AlN}$ 陶瓷在高密度封装技术中得到应用。

下面介绍本发明的实施例:

#### (一) 干压成型制备 $\text{AlN}$ 陶瓷基板

以平均粒径为 $2.5\mu\text{m}$ , 氧含量 $\leq 1.1\text{wt}\%$ , N含量 $\geq 33.3\text{wt}\%$ , C含量 $\leq 0.03\text{wt}\%$ 的 $\text{AlN}$ 混合料为原料, 加入一定量的 $\text{Y}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ 或 $\text{Dy}_2\text{O}_3$ - $\text{CaO}$ - $\text{Ga}_2\text{O}_3$ 等混合助烧结剂, 详细配方见表1。

表1.  $\text{AlN}$ 陶瓷的配方、烧成制度及热导性质

试样号	配方组成 (wt%)						粘结剂		烧成制度		热导率
	$\text{AlN}$	$\text{Y}_2\text{O}_3$	$\text{Dy}_2\text{O}_3$	$\text{CaO}$	$\text{Ga}_2\text{O}_3$	$\text{B}_2\text{O}_3$	PVA	PVB	温度 $^{\circ}\text{C}$	保温时间(h)	( $\text{W/m}\cdot\text{K}$ )
1	96	1.6	/	/	/	2.4	0.04	/	1800	4	189
2	96	2.0	/	/	2.0	/	/	0.035	1750	4	137
3	94	1.0	2.5	/	/	2.5	/	0.05	1650	4	146
4	94	/	3.2	1.0	1.8	/	/	0.04	1650	4	156

在配制好的料中加入无水乙醇、经48小时球磨混合后, 按常规的陶瓷制备工艺经烘干、过筛、加入少量的聚乙烯醇(PVA)或聚乙稀缩丁醛(PVB)作粘合剂混匀、造粒后, 利用干压成型法压制成所需形状和尺寸的

素坯。素坯必须经过排胶,排胶在气氛炉中进行,从室温至600℃在空气中进行排胶,升温速度视基板素坯厚度不同控制在0.4~0.6℃/min,600℃~1150℃在流动N<sub>2</sub>气保护气氛中进行,升温速度控制在2~3℃/min。

将排胶后的AlN素坯置于石墨炉中,以流动N<sub>2</sub>气等作保护进行烧结,烧结温度及保温时间,产品的热导率见表1。

## (二) 流延法成型制备AlN陶瓷基片

以平均粒径为2.0μm,氧含量≤1.0wt%,N含量≥33.3wt%,C含量≤0.03wt%的AlN粒体为原料,加入一定量的Dy<sub>2</sub>O<sub>3</sub>-CaO-Ga<sub>2</sub>O<sub>3</sub>或Dy<sub>2</sub>O<sub>3</sub>-CaO-B<sub>2</sub>O<sub>3</sub>等混合助烧结剂,详细配方见表1,按常规工艺在配制好的混合料中加入溶剂、分散剂、粘结剂和增塑剂制成流延浆料,浆料混合时间24~48小时,配方见表2。

利用流延成型机将浆料流延成所需厚度尺寸的坯带后切成一定尺寸的片状素坯,然后在气氛炉中按常规工艺进行排胶,其中从室温至600℃在空气中进行排胶,升温速度控制在0.2~0.3℃/min,600℃~1150℃在流动N<sub>2</sub>气保护中进行素烧,升温速度控制在2~3℃/min。

将排胶后的流延AlN素坯置于石墨炉中,以流动N<sub>2</sub>气等作保护进行烧结,烧结温度为1650℃,保温4小时,产品的热导率见表2。

表2. 流延AlN陶瓷的配方及热导性质

试 样 号	混合料配方组成 (wt%)					流延浆料配方组成 (wt%)								热导率	
	AlN	Dy <sub>2</sub> O <sub>3</sub>	CaO	Ga <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	溶 剂			分 散 剂		增 塑 剂		粘 结 剂		
						乙醇	环己酮	乙-丁酮	三油酸甘油酯	鱼油	1 <sup>#</sup>	2 <sup>#</sup>			
1	94	3.5	1.5	2.0	/	59.6	/	33	/	1.2	/	/	0.8	PVB	135
2	94.5	4.0	1.0	0.5	/	50.3	/	/	40.5	/	2.3	/	1.1	5.8	125
3	94	3.6	0.5	/	1.4	58.5	/	34	/	1.2	/	0.7	/	5.6	130
4	94	4.0	1.0	/	1.0	57.3	18	/	17	/	1.25	1.2	/	5.25	140
5	95	3.0	2.0	/	/	55.8	16.8	18.2	/	/	1.4	/	1.2	6.6	123

1<sup>#</sup> 二丁基钛酸盐  
2<sup>#</sup> 邻苯二甲酸二丁酯